Chiral DNA Nanopyramids of Gold

The research group of Senior Faculty Scientist Paul Alivisatos has harnessed the "self-assembly" methods that living systems use to construct the classic DNA "double helix" in order to make metal/DNA nanostructures which are chiral. The work was featured on the cover of the June 29, 2009 issue of the *Journal of the American Chemical Society*.

The ability of two single strands of DNA with complementary sequences (A–T and G–C) of their linearly arranged "bases" (adenine, thymine, guanine, cytosine–ATGC) to spontaneously bind each other with precise three-dimensional control is the chemical basis of most life on earth. Use of this molecular machinery in combination with synthetic chemistry is therefore an attractive method for building nanoparticle assemblies with unique properties.

The LBNL-developed "DNA-templated" nanostructure assembly technique involves first, the binding of gold nanoparticles to single strands of DNA using a thiol (sulfur atom) linker. Subsequent self-directed assembly of two complementary gold-carrying DNA strands creates the double helix structure which precisely locates the nanoparticles at predetermined distances from each other, based on the length of the DNA pieces. Over the last decade, researchers around the world have extended this approach to form discrete DNA nanostructures with a variety of more complex non-linear geometries including triangles, pyramids, cubes, and more intricate polyhedra.

In this work, another major advance has been made in the field: the creation of "chiral" nanostructures–identical mirror-imaged (right and left-handed) forms of DNA carrying nanocrystals. The importance of chirality is clearly seen in the fact that the majority of biologically important molelcules are chiral.

The chiral pyramid design developed here used four strands of DNA, each of which bends twice to form one of the four faces of a pyramid. Chirality was achieved by placing a differently sized gold nanocrystal (5, 10, 15, or 20 nm) on the end of each DNA strand. For proper self-assembly each third of each strand was constructed to be complementary to one third of another strand (see figure). The strands were designed with three thymine or adenine bases (T–A) at the corners of the pyramid to allow sufficient flexibility for the molecule to make that turn. Also, the terminal three base pairs of each strand have the stronger binding guanine or cytosine (GC), to reduce fraying at the ends. For the R (right handed) "enantiomer", a 5 nm particle was put on strand 1, a 10 nm particle on strand 2, a 15 nm on strand 3, and a 20 nm on strand 4. To construct the S enantiomer (left handed), the positions of the 5 and 10 nm particles were simply switched. Transmission electron microscopy clearly showed the successful formation of the pyramids.

The "construction" of discrete and chiral nanostructures demonstrated here is not limited to those carrying gold. A wide variety of linker moieties are readily available for synthetic DNA, allowing linkage to many nanoparticle materials. Additionally, the ends of the DNA strands are available for further functionalization, either with additional chemical linkers or simply with trailing "sticky ends" of single stranded DNA that are available to bind other pieces of DNA with the appropriate base sequence. This might allow these assemblies to be immobilized on surfaces or incorporated into larger structures, such as self-assembled DNA tiles.

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Alexander J. Mastroianni, Shelley A. Claridge, and A. Paul Alivisatos, "Pyramidal and Chiral Groupings of Gold Nanocrystals Assembled Using DNA Scaffolds," J. Amer. Chem. Soc., 131, 24, (8455-8459) 2009.

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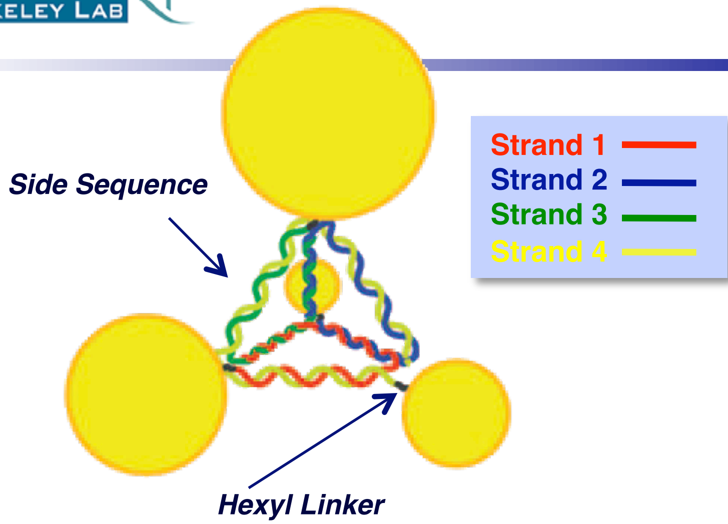
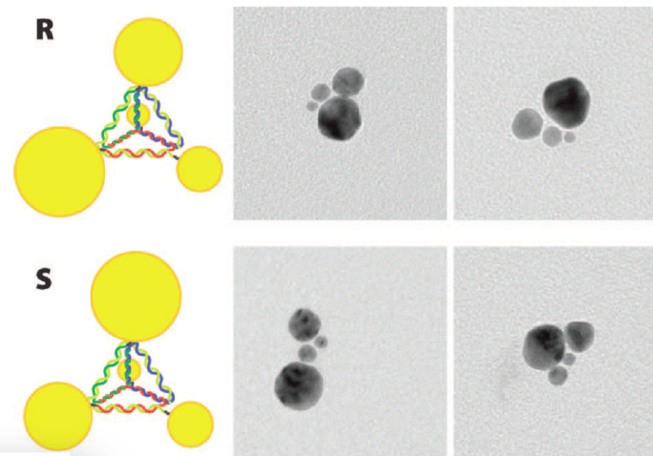
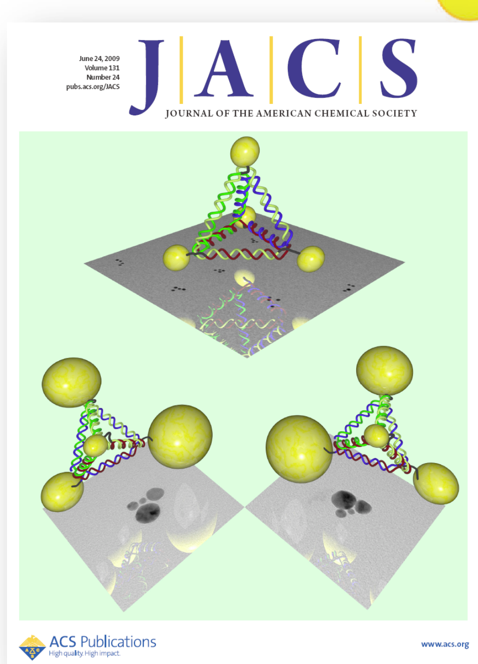
Chiral Nanopyramids of Gold





Four strands of single stranded DNA self assembled *to form a nanopyramid with gold nanoparticles at the vertices. Each DNA strand bends to create the three pyramid sides tracing out one face of the pyramid. The strands were designed to sufficiently flexible to form into a compact pyramid.*



Chiral pyramids were synthesized *by placing a differently sized gold nanocrystal on the end of each strand (schematic, left). For the R enantiomer (right handed) a 5 nm particle was used on strand 1, a 10 nm on strand 2, a 15 nm on strand 3, and a 20 nm on strand 4. The S enantiomer (left handed) was constructed by a simple switch of the position of the 5 and 10 nm particles. Transmission electron microscopy clearly showed the successful formation of the pyramids (images on right).*